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ATMOSPHERIC PRESSURE CHEMICAL IONIZATION

NEGATIVE MASS SPECTRA OF THE

DINITROTOLUENE ISOMERS

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by

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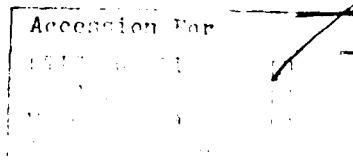Québec, Canada   May/mai 1981

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RESUME

L'ionisation chimique à pression atmosphérique des isomères
du dinitrotoluène (DNT) a été étudiée dans l'air ambiant, à l'aide
d'un spectromètre de masse quadripolaire opérant dans le mode négatif.
Les isomères sont regroupés sur la base des ions produits: le 2,5-,
le 2,6- et le 3,5-DNT forment l'anion moléculaire avec peu de fragmenta-
tion; le 2,3- et le 3,4-DNT se comportent de façon similaire mais
avec beaucoup plus de fragmentation; le 2,4-DNT produit l'ion quasi-
moléculaire (DNT-H)$^-$ avec très peu de fragmentation. Les résultats
sont interprétés en termes de structure moléculaire des isomères. (NC)

ABSTRACT

The atmospheric pressure chemical ionization of the
dinitrotoluene (DNT) isomers in ambient air was studied with a quadrupole
mass spectrometer operating in the negative mode. The isomers can
be grouped on the basis of the product ions: the 2,5-, the 2,6-,
and the 3,5-DNT give the molecular anion with little fragmentation;
the 2,3- and the 3,4-DNT behave similarly but with more extensive
fragmentation; the 2,4-DNT gives the quasimolecular (DNT-H)$^-$ with
little fragmentation. The results are discussed in term of the molecular
structure of the isomers. (U)

Accession For

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1.0 INTRODUCTION

Technologies of trace gas analysis based on the chemical ionization phenomena are presently our best hope to develop instruments capable of detecting the explosives vapors that emanate from bombs or explosive stock. Among the instruments available, the atmospheric pressure chemical ionization (APCI) mass spectrometer offers a high sensitivity and the best specificity (the most certain identification of the detected chemicals). Furthermore, this type of instrument provides an excellent means of studying chemical ionization at atmospheric pressure. This phenomenon is best described by the ion-molecule reactions involved.

The ion-molecule chemistry encompasses all reactions leading to the formation of the ions detected (products ions). These reactions take place between the molecules and the reactant ions which, under some conditions, may include thermal electrons. The nature of the reactant ions depends both on the carrier gas and on the type of ionization source employed. Before attempting a complete quantitative description of the chemical ionization process, it is essential to understand the influence of the molecular structure. In our study, this was done by comparing the behavior of the six dinitrotoluene (DNT) isomers.

DNT was studied because it is the molecule offering the best hope to detect military grade TNT since it has a relatively high vapor pressure (Ref. 1) and is always present in military grade TNT (Refs. 2 and 3). To keep the experiments simple and as similar as possible to a real-time detection scenario, air was used as the carrier gas. A corona-discharge source provided primary ionization.

This work was performed between March and November 1979, under PCN 21E01, Explosives Detection Technology, now PCN 21A07.

2.0 EXPERIMENTAL

The chemical ionization of the isomers and the analysis of
the product ions was performed with a Trace Atmospheric Gas Analysis
system, TAGA 3000 (Trade Mark of Sciex Inc., Toronto), developed under
contract for DND. This instrument is characterized by its high
sensitivity, its ability to sample directly from ambient air at high
flow rate, and its high speed cryogenic vacuum system.

The TAGA system is based on quadrupole mass spectrometer technolo-
gy; it has a highly efficient atmospheric pressure chemical ion source.
The unique interface between the vacuum section and the ionization
region assures an efficient and trouble-free passage of the ions from
the ionization source to the heart of the mass spectrometer. Figure 1
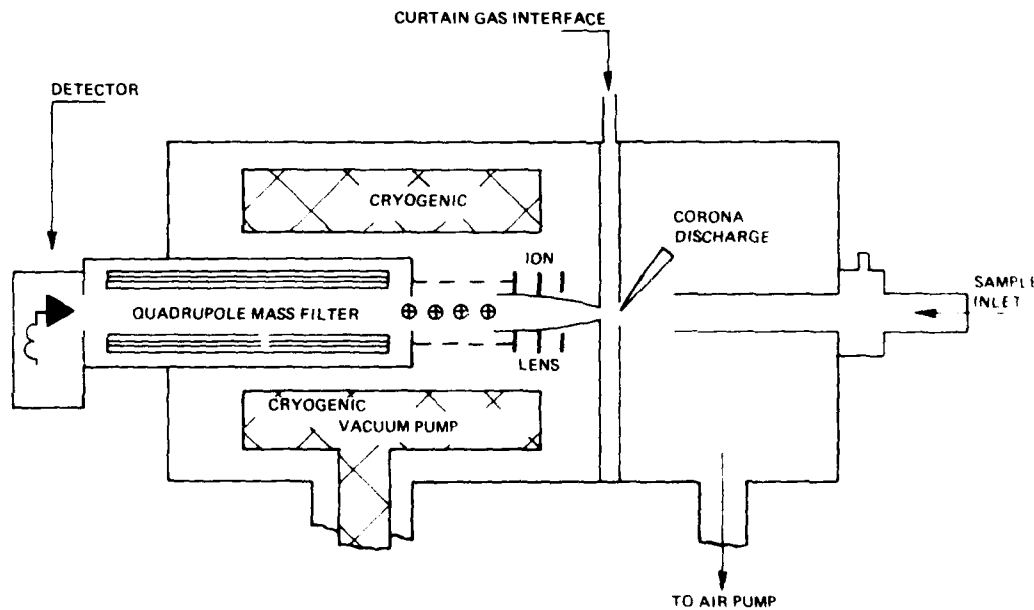shows a diagram of this instrument.

FIGURE 1 - Diagram of the TAGA 3000 Mass Spectrometer

A point-to-plane corona-discharge source initiates and sustains the atmospheric pressure chemical ionization. An electric field is used to rapidly select the polarity of the ions to be studied and to draw them to the atmospheric pressure/vacuum interface. A dry inert gas (nitrogen) flows between the two main plates of this interface. This gas blows out any particulate and vapor that might enter the ionization source region, thus preventing any clogging of the atmospheric pressure/vacuum orifice; it also reduces the clustering effect encoutered in the free-jet expansion of the ion-air mixture into the vacuum (Ref. 4). In vacuum ion lenses focus the positive or negative ions into a quadrupole mass filter for analysis and pulse counting detection. A powerful microprocessor interactionally controls the system via a CRT graphics terminal; it also performs data acquisition, treatment and storage. This microprocessor is supported by a hard copy unit and a dual floppy disc unit; its control can be completely or partially overridden for manual operation if desired. Detailed specifications are given in Appendix A.

All the DNT isomers, except the 3,5-DNT, were from K & K Laboratories (New-York); they were all recrystallized twice. Purity was ascertained by the melting point (Table I) and by gas-liquid chromatography, using an "Ultrabond" column 1/8 in in diameter, 6 ft long, at 418 K. The carrier gas was nitrogen flowing at 40 mL/min. The chromatograph was a model 550 from Tracor Inc.; this instrument was equipped with an electron capture detector. The measured retention times are presented in Table I.

Following the method described in Ref. 5, to which we brought minor changes, we synthesized the 3,5-DNT by diazotation of 4-amino-3,5-dinitrotoluene. This last compound was obtained by the nitration of N-acetyl-p-toluidine purchased from K & K Laboratories, Inc. (New York). The details are given in Appendix B.

TABLE I

DNT Isomers

Isomers	Melting Point* (K)	Retention Time (s)	Concentration in Air Flow (ppb)
2,3-DNT	334(334.2)	292	40
2,4-DNT	344(343.3)	221	43
2,5-DNT	325(325.7)	184	47
2,6-DNT	338.5(339.2)	150	62
3,4-DNT	333(333.0)	457	56
3,5-DNT	365.5(366.2)	210	56

* (Litt.)

Each isomer was dissolved in glass distilled methanol and injected continuously in the flow (39 L/min) of ambient air, 40 cm ahead of the corona discharge, with a 10-mL syringe pump (Sage Instrument, Model 355). The wall of the 22-mm glass tube leading to the ionization source was heated outside the source assembly, at about 425 K, but the temperature at the middle of the source never exceeded 333 K; the wall of the TAGA 3000 ionization source was stabilized at about 313 K. To eliminate the formation of drops at the end of the needle, its tip was made to touch a small piece of ground glass placed in the middle of the 22-mm tube. The injection rate, 16.8 uL/min, produced a stable concentration of about 50 ppb,

which was sufficient to emit strong signals. The exact concentration
of each isomer is given in Table I. This inlet glass system was cleaned
and a blank test was run between each new isomer analysis. The relative
ambient humidity was always between 45 and 52 percent.

Furthermore, the 2,4-DNT was studied in pure nitrogen (Linde,
ultra high purity). One gram of purified 2,4-DNT was placed in a
clean tube designed like a vacuum trap and above which purified nitrogen
was circulated at 2 L/min. This tube was heated with a sandbath
thermostatted at 325 K. Because of the small carrier flow, a 4-mm
I.D. inlet tube was used instead of the usual 22-mm one, and the
curtain gas flow rate was increased to 350 mL/min. The ambient source
housing was also purged with another 1 L/min flow of the same nitrogen.

It must be noted that these experiments were not performed
to determine the ultimate sensitivity of the TAGA 3000 to DNT. There
was considerable loss of sample on the surface of the inlet and ioniza-
tion source which had to be cleaned between samples; the instrument
was not adjusted for high sensitivity but rather for good resolution.

For each isomer, the mass spectra were repeatedly scanned over
the mass ranges 15-90, 80-180 and 150-250 amu, at a speed chosen to
guarantee a 90% probability of ion current error inferior to 5% on
the peak intensities. All data were stored on floppy discs, examined
scan by scan, averaged, and tabulated.

The controlled parameters of the TAGA 3000 mass spectrometer
chosen for these experiments are shown in Table II.

TABLE II

Control Settings of the TAGA 3000

Corona discharge	:	-0.63 µA
Interface voltage	:	-470 V
Lens 1	:	-30 V
Lens 2	:	-13 V
Lens 3	:	10 V
Lens 4	:	150 V
Lens 5	:	-14 V
Rod Offset	:	-12 V
Resolution parameter	:	148
Multiplier	:	4650 V
Air motor parameter	:	0.575
Threshold	:	30 ions/s
Peak parameter	:	2415154 and 2205050
Curtain gas	:	250 mL/min; nitrogen
Operating pressure	:	2.6×10^{-6} torr

3.0 RESULTS

The absolute intensities of all the anions significant peaks
are listed in Table III, for the six DNT isomers and for a typical
background of the laboratory ambient air recorded under the same con-
ditions.

For the ions having a mass below 70 amu, the intensity values
should be interpreted with caution as only large intensity variations
are significant. This is so when the carrier gas is the laboratory
ambient air whose humidity and impurity content is not controlled.
Under such conditions, hourly fluctuations in the intensities of
the light anions are expected, particularly for mass 32 $[O_2^-]$,
46 $[NO_2^-]$, 50 $[O_2^-(H_2O)]$, 60 $[CO_3^-]$, 61 $[HCO_3^-]$, 62 $[NO_3^-]$, 64 $[SO_2^-$
and $O_4^-]$, and 68 $[O_2^-(H_2O)_2]$.

Figures 2 to 7 represent the mass spectrum of the six isomers
with the intensities normalized to either mass 182 (DNT^-) or 181,
depending on which was the more intense after background subtraction.
This presentation was chosen because of some important variations
in the intensities of the light anions which in some cases, exceed
those of m/e 181 or 182. Intensities exceeding 100% of the base
peak (181 or 182) have been divided by 10 in the graphical representation.

To facilitate the comparison of the ionization behavior of
the isomers, the most significant peaks used in the discussion are
listed in Table IV with a diagram indicating the relative positions
of the nitro substituents.

TABLE III

Chemical Ionization Mass Spectra of the DNT Isomers in ions/s

| m/e	2,3-DNT	2,4-DNT	2,5-DNT	2,6-DNT	3,4-DNT	3,5-DNT	Laboratory Air
31	18600	32748	12820	10500	23094	4500	19196
32	49256	60992	42088	85808	79728	104176	187392
35	13288	514	248	2836	276	4669	373
37	4332	24	103	1027	233	1469	135
45	32400	11008	4506	16102	10707	16926	11346
46	212384	24220	29788	35624	49525	43208	30956
49	15808	43800	35936	26696	55189	100192	2700
50	54328	103280	116460	233504	104757	322240	255712
52	157	580	630	1911	2229	2305	0
53	2737	142	92	1495	93	2923	0
59	23992	3600	51288	33296	20597	15900	20960
60	116144	76960	117856	171936	67659	119072	83384
61	25316	24860	30496	47616	25327	43408	39112
62	12168	2400	5076	4546	6055	3092	2260
63	0	0	1048	0	693	7268	0
64	26620	8073	9970	12728	10544	29908	6944
67	508	9356	145	0	240	8400	0
68	4512	15436	13260	51280	20393	76064	53360
73	174	796	463	1671	900	1539	1566
75	4539	1374	3580	2423	1894	2066	0
76	12238	2735	7842	11426	5892	16394	6284
77	24576	30668	18439	13172	18717	9487	5722
78	2480	4790	5016	7736	3204	13490	8355
79	11556	6491	9282	16346	5963	17578	8364
82	555	827	1086	2272	1217	3077	173
86	0	0	145	1777	281	1925	1433
89	6474	3880	2381	6423	1697	3994	2803
92	11213	9662	8784	14890	10500	28436	17672
94	3724	4331	4787	8644	3481	8937	10396
96	463	833	780	1993	1412	4903	2534
115	1091	1011	512	1055	1146	1519	1698
152	894	410	3163	1503	1620	2818	185
167	58	186	57	82	27	37	44
168	2863	79	184	136	10257	677	76
181	56	54587	0	0	183	51	103
182	14535	7848	58572	65280	17992	42280	56
183	1068	828	4411	3332	1284	3987	46
197	124	429	15	316	1280	1380	51
198	58	163	796	80	132	651	39
212	2489	44	52	108	708	82	20
228	976	58	13	54	369	840	17
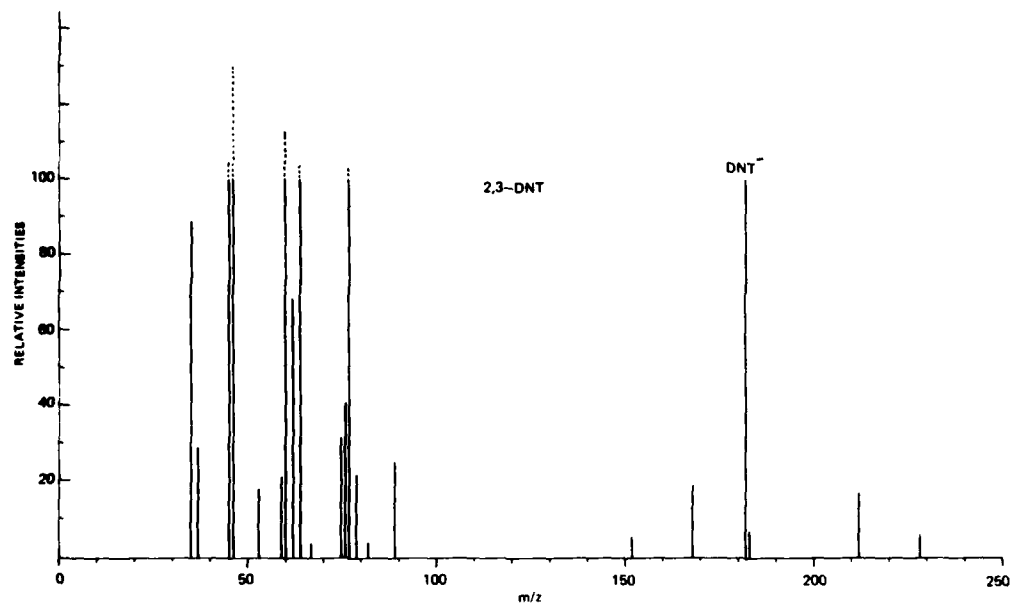
FIGURE 2 - Mass Spectrum of 2,3-DNT
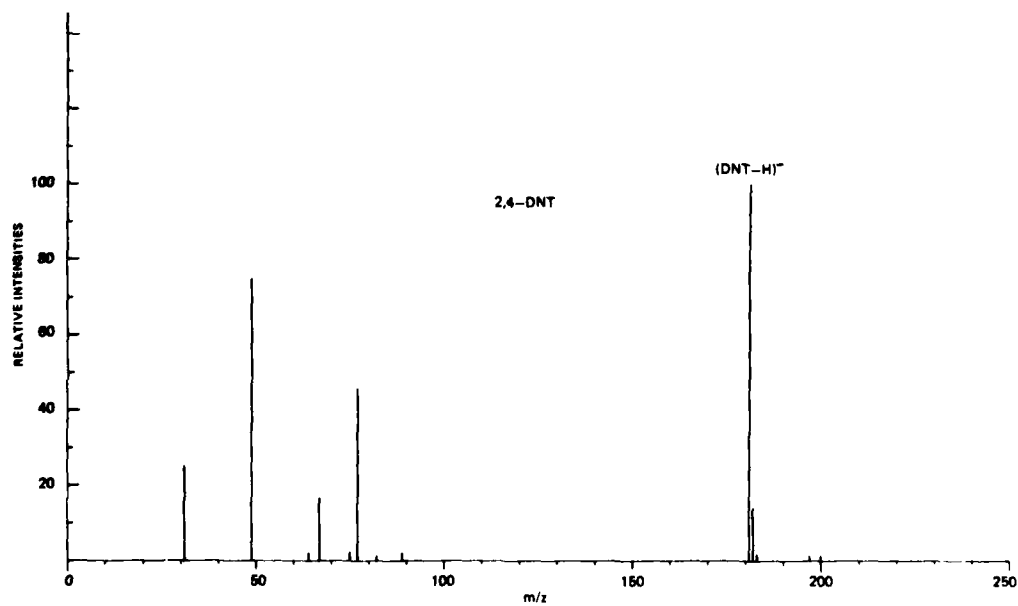
FIGURE 3 - Mass Spectrum of 2,4-DNT

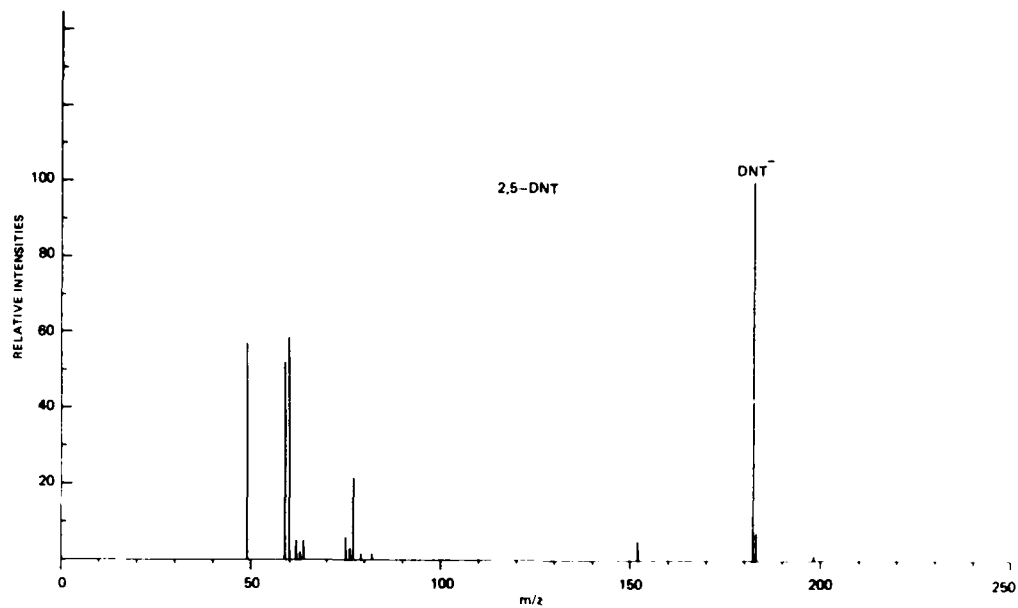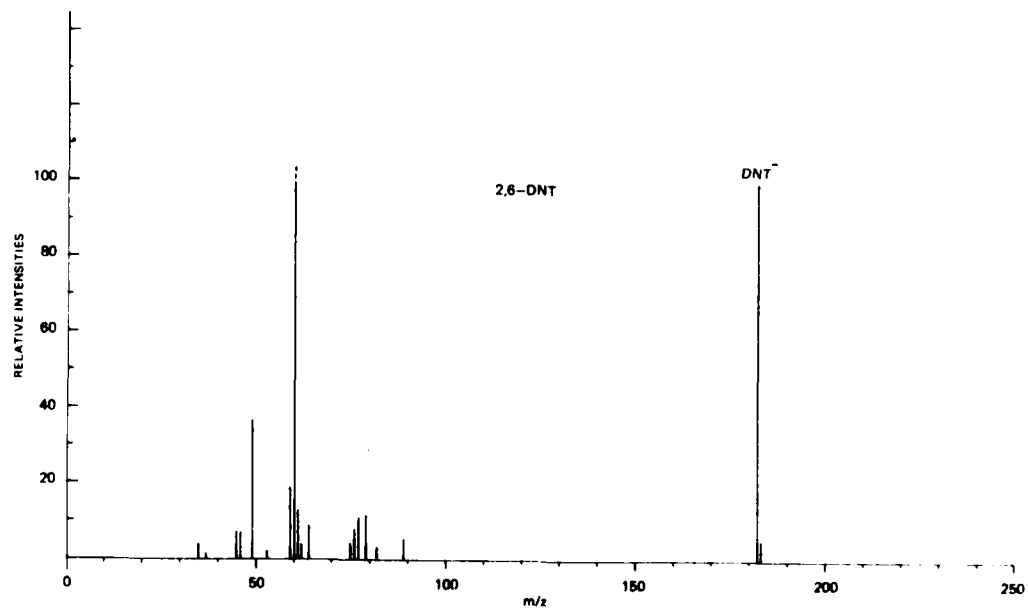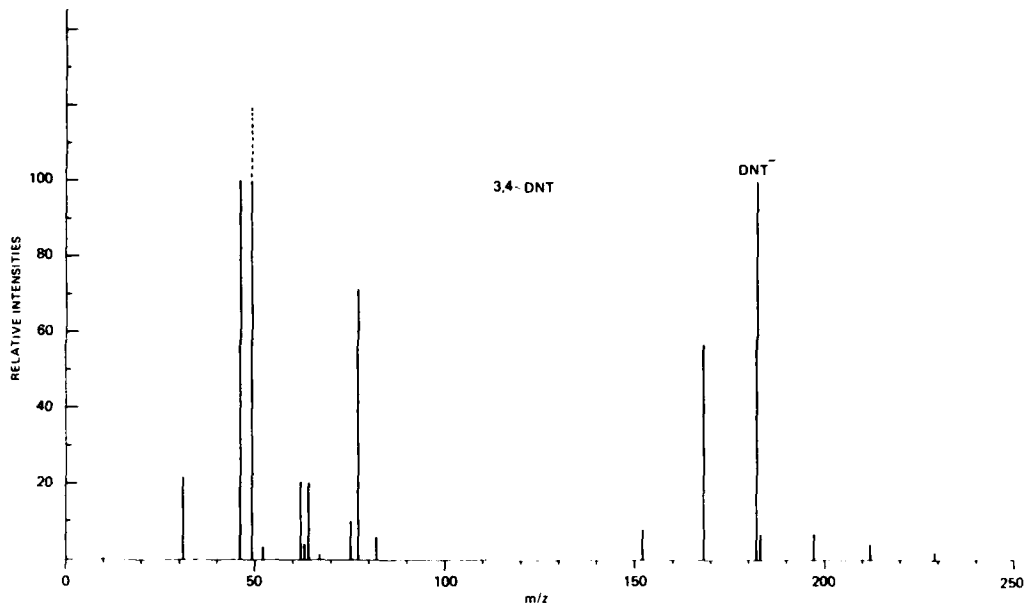FIGURE 4 - Mass Spectrum of 2,5-DNT

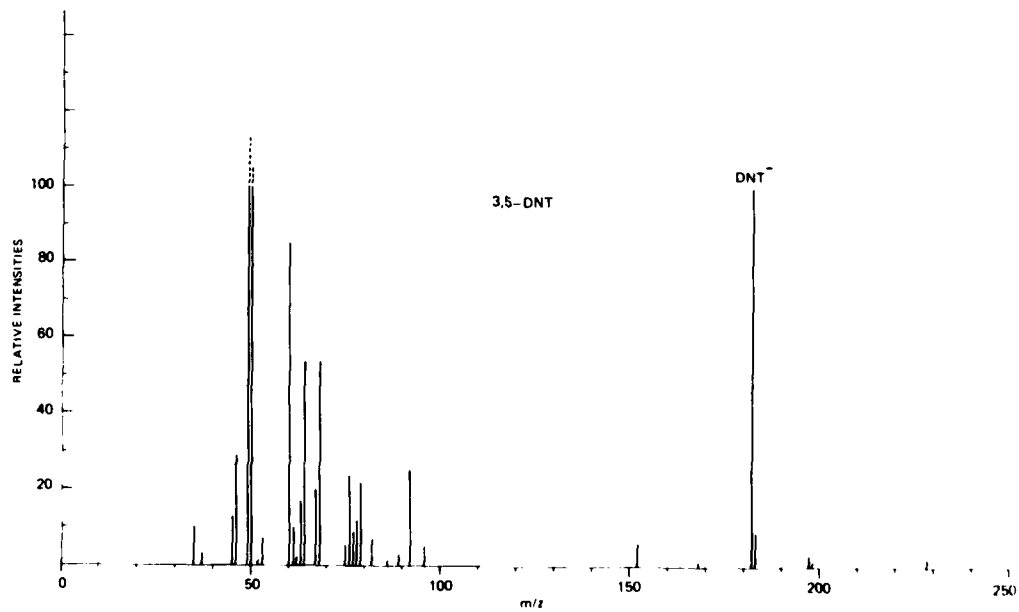FIGURE 5 - Mass Spectrum of 2,6-DNT
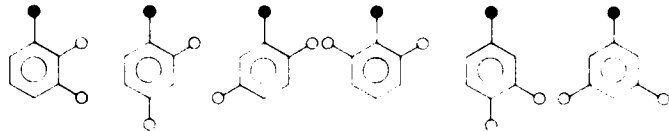
FIGURE 6 - Mass Spectrum of 3,4-DNT

FIGURE 7 - Mass Spectrum of 3,5-DNT

TABLE IV

Intensities of the Most Significant Peaks in Ions/s

m/e	2,3-DNT	2,4-DNT	2,5-DNT	2,6-DNT	3,4-DNT	3,5-DNT
46	212384	*	*	*	*	*
152	894	410	3163	1503	1620	2818
167	58	186	5⁻	82	2⁻	3⁻
168	2863	79	184	136	1025⁻	6⁻⁻
181	56	54587	0	0	183	5151
182	14535	⁻848	585⁻2	65280	1⁻992	42280
19⁻	124	429	15	316	11280	1380
198	43	204	1009	⁻6	116²	652
212	2489	44	5²	108	⁻08	8²
228	97b	58	13	54	3b9	840

*: Close to the background value (31 000)

● : CH_3

O : NO_2

When reading the intensities of the ions from Table III or IV it must be remembered that the isotopic distribution of each element of the ions must be taken into account. Naturally occurring carbon contains 98.89% of C^{12} and 1.11% of C^{13}, nitrogen is mostly N^{14} but there is 0.37% of N^{15}, while oxygen has 0.037% of O^{17}. A given ion will have its principal contribution at, say, mass M amu, bu⁺ the same ion will also contribute at mass M+1 amu (contribution to mass above M+1 can be ignored here). For example, Table III shows that 2,4-DNT produces a strong peak at 181 amu, which corresponds to DNT minus a hydrogen atom (DNT-H)⁻. The same ions (DNT-H)⁻ contributes 8.66% of its total intensity to mass 182, and 91.34% to mass 181 because it has seven carbon atoms, two nitrogen atoms, and four oxygen atoms.

Thus, from the 7 848 ions/s observed at 182 for 2,4-DNT about
5 175 ions/s are $(DNT-H)^-$ and 2 700 are DNT^-.

The abundance of fragment ions of 2,3-DNT and 3,4-DNT is
remarkable, particularly for 2,3-DNT which produces a very strong
NO_2^- peak at 46 amu.

In Table V, the mass spectra of 2,4-DNT, was run in pure nitro-
gen, are reported for two values of the electrostatic lens L1. The
potential difference L1-L2, also called the cluster-breaker potential
(expressed in volts over a distance of about 3mm), can sufficiently
increase the kinetic energy of the ions to induce some declustering
by causing collisions in this region where the pressure is still relative-
ly high (about 0.1 mm of mercury). If this value is increased from
30 to 50 V, the intensity of O_2^- at 32 amu is increased and the
intensities of $O_2(H_2O)^-$ at 50 amu and of $O_2(H_2O)_2^-$ at 68 are decreased.
The intensity of the molecular ion DNT is thus nearly doubled, possibly
because of the higher reactivity of O_2^- compared to its clustered
homologues.

4.0 DISCUSSION

4.1 Ion-Molecule Reactions in the Negative Mode

In ambient air, the APCI of DNT occurs in a dilute plasma con-
taining many ionic species. The important anions detected in pure
air are listed in the last column of Table III, under "Laboratory
Air". These are the negative mode reactant ions. Also contributing
to the ionization medium is an unknown quantity of thermalized electrons.
All these ionic species may react with the molecules studied, often
in a complex way, since atmospheric pressure enhances three-body
collisions. In such a situation, characterizing the different ion-
molecule reactions taking place by sorting out the reactant and product

TABLE V

Significant Anions of the Mass Spectra of 2,4-DNT in Nitrogen

| m/e	L1 = -30 V	L1 = -50 V
	ions/s	
46	352	3611
136	57	239
152	301	1114
165	202	1265
166	386	547
181	268	0
182	10944	19856
183	1053	1806
184	135	295
196	371	110
198	130	35
215	28	114
225	119	48

ions is difficult. Before analyzing the results, it is desirable to review the typical processes responsible for the formation of anions.

4.1.1 Direct Charge Transfer

$$\text{Example:} \quad O_2 + NO_2 \rightarrow NO_2^- + O_2 \qquad [1]$$
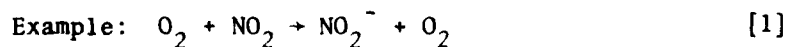
The transfer of the electron is governed by the anion with the highest electron affinity (EA). In this example the electron affinity of oxygen is less than that of NO_2 (EA (O_2) = 0.48 eV and EA (NO_2^-) > 2.04 eV (Ref. 6).

In some cases, dissociation follows:

$$\text{Example: } O_2^- + HCCl_3 \rightarrow Cl^- + HCCl_2 + O_2 \qquad [2]$$
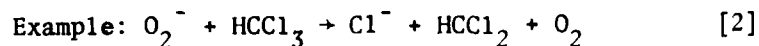
where EA (Cl^-) = 3.61 eV. This is oftem the case when the EA difference is large.

4.1.2 Proton Transfer

$$R_1H + R_2^- \rightarrow R_2H + R_1^- \qquad [3]$$
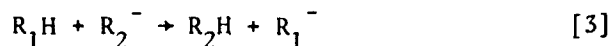
The gas phase acidities of R_1H and R_2H govern this type of reaction. $D(R_1-H)$ being the dissociation energy of the bond, R_1-H, the gas phase acidity increases when the difference:

$$D(R_1-H) - EA (R_1)$$

decreases,

$$\text{Example: } \qquad O_2^- + NO_2C_6H_4OH \rightarrow NO_2C_6H_4O^- + HO_2 \qquad [4]$$
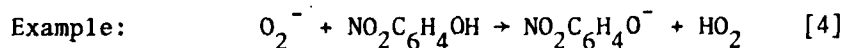
$$D(H-O_2) - EA(O_2^-) = 2.04 \text{ eV} - 0.48 \text{ eV} = 1.55 \text{ eV}$$

and
$$D(NO_2C_6H_4O-H) - EA (NO_2C_6H_4O^-) = 3.83 \text{ eV} - 3.2 \text{ eV}$$
$$= 0.6 \text{ eV}$$

O_2^- is an important base' its conjugate acid, HO_2, is a stronger gas phase acid than phenol, but it is weaker than acetic acid (Ref. 7).

4.1.3 Attachment and Clustering

Attachment or clustering is exemplified by the process:

$$X^- + Y \rightarrow XY^- \qquad\qquad [5]$$

where X^- can be Cl^-, Br^-, NO_2^-, NO^-, O_2^-, OH^- ..., and Y often is water or another large molecule.

$$\text{Example:} \quad O_2^- + nH_2O \rightarrow O_2^-(H_2O)_n \qquad [6]$$
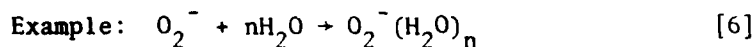
$$n = 1,2,3,...$$

In our instrument, large clusters are not sufficiently stable to survive transport through the curtain gas which protects the vacuum section. Clusters can also be broken, and thus identified, by increasing the voltage difference between lenses 1 and 2 so that the accelerated clusters will collide and dissociate.

4.1.4 Thermal Electron Capture

If a carrier gas, free of oxygen as well as of other molecules with a high EA is used (nitrogen, helium, argon), the direct capture of thermalized electron by the solute becomes the principal source of product anions. This occurs according to reactions [7] or [8].

$$e^- + AB \rightarrow AB^- \qquad\qquad [7]$$

$$e^- + AB \rightarrow A^- + B \qquad\qquad [8]$$

The probability of electron capture is controlled by the EA and the collision cross section of the molecules. When air is the carrier gas, nearly all electrons are captured by O_2 via reaction [7] and, because of its high reactivity and low mobility, O_2^- is subsequently engaged in processes [1] and [4].

Table III shows that the principal reactant-ions combining with DNT are O_2^- at 32 amu, $O_2^-(H_2O)$ at 50 amu, and $O_2(H_2O)_2^-$ at 68 amu; this is indicated from their intensity which is lower than the background expect for the 3,5-DNT where the intensity of masses 50 and 68 actually increased for some unknown reason.

The study of the product ions is best done by dividing the DNT isomers into three groups.

4.2   The 2,5-, 2,6-, and 3,5-DNT Isomers

The molecular ion, DNT^- at 182 amu is the principal product ion, with intensities between 42 000 and 65 000 ions/s and little fragmentation. The ionization of these DNT isomers is mainly caused by electron transfer from the superoxide anion O_2^- to the DNT. The high EA of nitro derivatives of benzene favors this transfer. The EA of each of the DNT isomers is not known but the following are indicative: m-dinitrobenzene: 1.43 eV (Ref.8), sym-trinitrobenzene: 1.86 eV (Ref. 8) and 2,4,6-trinitrotoluene between 2.8 and 3.2 eV (Ref. 7). Thus the electron transfer from O_2^- to DNT is due to the high EA of nitro-aromatic molecules.

4.3   The 2,3-, and 3,4-DNT Isomers

Again the molecular ion at 182 evidences the electron transfer from the superoxide anion, O_2^-, but its intensity, only 14 000 and 18 000 ions/s, is much lower than those of the 2,5-, 2,6- and 3,5-DNT. On the other hand, Table IV shows that the fragmentation is much higher. Particularly for 2,3-DNT, the most intense product ion is NO_2^- at 46 amu; this indicates extensive fragmentation. For 3,4-DNT the intensity intensity of product ion at 168 amu is 57% of the molecular ion and it represents the net loss of a nitrogen atom, possibly by NO_2^- replacement with O_2^-. This important fragmentation of the 2,3- and 3,4-DNT

is explained by the lower stability of the molecular anions 2,3-
and 3,4-DNT.

An important factor for the stability of aromatic molecules
is the resonance energy gained by the delocalization of the Π-electron
system. This effect is operative in the molecule and in the product
ion. In the 2,3- and 3,4-DNT there is a particularly strong steric
inhibition to resonance because of the large tilt angle of the nitro
groups due to their steric interactions. The electronic transitions
provide a good measure of the extent and shape of the Π-electrons
systems. The first transition is 210.0 nm for 2,3-DNT and 219.0 nm
for 3,4-DNT, which is close to that of benzene itself. On the other
hand, the four other DNT isomers absorb between 240.0 and 265.5 nm
indicating that for 2,3- and 3,4-DNT, both nitro groups are significantly
out of plane with the benzene ring (Ref. 9). The effect of the tilt
angle of NO_2 on the resonance energy has been calculated (Ref. 10) for
nitrobenzene: for the perfect planar configuration, the resonance
energy due to a nitro group is -27.2 kJ/mole, whereas for a 40° tilt
angle it is -15.5 kJ/mole, and only -4.1 kJ/mole for a 60° tilt angle.
A similar loss of resonance energy by steric inhibition in the 2,3-
and 3,4-DNT molecules and the additional tension arising from the
ortho NO_2 - NO_2 repulsion are responsible for the lower stability
of the molecular anion DNT⁻ and the fragmentation observed. The
enthalpy of formation of the isomers (Ref. 11) is also a good indication
of the importance of the resonance energy for the stability of the
molecules: 2,3-DNT, -87.4 kJ/mole; 3,4-DNT, -80.3 kJ/mole; 2,5-DNT,
-188.3 kJ/mole; 3,5-DNT, -238 kJ/mole; 2,6-DNT, -241 kJ/mole, and
finally the most stable, 2,4-DNT, -374.5 kJ/mole.

4.4 The 2,4-DNT Isomer

This isomer is unique: it produces the quasimolecular anion
(DNT-H)⁻ at 181 amu and its contribution to the molecular ion (182 amu)

is very small, less than 5% of the 181 peak after correction for
the isotopic abundance. The lack of subsequent fragmentation observed
indicates a high stability for the quasimolecular anion at mass 181.
This particular behavior results from the combined action of the
two nitro groups to withdraw electrons from the benzene ring and
induce a positive charge on the methyl group. The acidity of this
methyl substituent permits a proton transfer (type 3 reaction) between
this group and the superoxide anion, O_2^-. We will now explain why
this reaction does not occur in any of the other DNT isomers.

When there is one of more nitro groups, the electron withdrawal
from the aromatic ring, that creates partial positive charges at
other locations, is caused by two mechanisms: the induction and the
resonance effects. The first effect is universal, in the sense that
its intensity will be the same whether the nitro substituent is ortho,
meta or para; it is generally weaker than the resonance effect (Ref. 12).
The latter effect will also create partial positive charges but only
in ortho and para positions if the nitro groups are nearly coplanar
to the aromatic ring.

A situation allowing a positive combined action of the resonance
and induction effects of both nitro groups is, at first sight, possible
only for the 2,4- and 2,6-DNT isomers. But a large steric effect
exists in the case of the 2,6-DNT because of the proximity of the
nitro-methyl-nitro substituants which prevents the contribution of
the resonance effect of one of the nitro groups. This is well
illustrated by the ultra-violet absorption spectra: the 2,4-DNT
absorbs at 252.0 nm, and the 2,6-DNT at 241.0 nm (Ref. 9). Thus
only for the 2,4-DNT will we have a concerted action of the two nitro-
groups sufficient to permit the abstraction of a proton.

Another mass spectrometry study also observed the acidity of
the methyl in 2,4,6-trinitrotoluene (Ref. 7) and in the 2,4-DNT isomer
(Ref. 13), but this phenomenon was not related to the detailed isomeric
structure of the molecules.

To confirm the proton acidity of 2,4-DNT and its reaction with
O_2^-, the mass spectrum of this isomer introduced in the gas phase was
run in pure nitrogen. The most significant peaks are reported in
Table V. The absence of proton abstraction is made evident by the
low intensity of mass 181 and the strong molecular ion peak at mass
182. The formation of this anion is due to nondissociative thermal
electron capture (type 7 reaction). This type of reaction was studied
in detail for ortho and meta nitrotoluenes (Refs. 14 and 15) with
the quasimonoenergetic electron swarm beam technique using a negative
ion mass spectrometer. It was found that a nondissociative electron
capture reaction occurs at about 0.04 eV and that a dissociative
capture, with loss of a NO_2^- group, occurs at about 1.0 and 3.5 eV,
the exact values depending on the isomers.

We finally noted that the DNT isomers all formed ion clusters,
with relatively low intensities. The following is a tentative
attribution: 197 amu $[DNT-H + O]^-$, 198 amu $[DNT + O]^-$, 212 amu
$[DNT + NO]^-$, and 228 amu $[DNT + NO_2]^-$.

5.0 CONCLUSIONS

The atmospheric pressure chemical ionization of all the DNT
isomers was studied in ambient air to probe the effects of their
small structural differences on the anions produced. A high sensitivity
quadrupole mass spectrometer, the TAGA 3000 (Sciex Inc., Toronto),
was used to characterize the product ions. A point-to-plane corona
discharge sustained the ionization phemonemon. We observed three
different types of behavior:

a)   the 2,5-, 2,6-, and 3,5-DNT isomers give a very intense molecular anion, DNT$^-$, at 182 amu, produced by an electron transfer from the superoxide anion, O_2^-;

b)   the 2,3- and 3,4-DNT isomers also give the molecular anion DNT$^-$, at 182 amu but, contrarily to the first grou, this phenomenon is accompanied with extensive fragmentation. This is because of the lower resonance energy of the Π-electron system occasioned by the ortho NO_2 - NO_2 steric hindrance.

c)   the 2,4-DNT isomer, the most important one for TNT detection, mostly produces the quasimolecular ion (DNT-H)$^-$ at 181 amu and the fragmentation is negligible. This unique behavior is caused by the acidity of the methyl group which permits the transfer of a proton to the superoxide anion, O_2^-. In pure nitrogen, where basic anions are absent, 2,4-DNT behaves like the isomers of group 1.

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APPENDIX A

SPECIFICATIONS OF THE DND TAGA 3000

Front End Modules

1. Ambient Air Analysis Front End

    Allows some variation of the APCI source geometry and operation at flow rates up to 500 L/min. It is ideal for ambient air analysis.

2. Temperature Controlled Dual Discrete Sample/Continuous Sample Front End

    It operates between 298 and 498 K, and the chosen temperature is stabilized by a digital controller. The flow-control network permits operation between 30 and 600 mL/min. It also features a septum-less injection port for the analysis of microlitre volumes of discrete liquid or vapor samples.

Vacuum System

Roughing Pump
Alcatel Inc.,   It shuts off below 8 X 10^{-5} torr.
Model 2008A

Cryopump   A two stage Air Product Inc., Model CSA-202, helium cryo-refrigerator attached to the cryo-shell. Pumping speed: 20 000 L/min at 10^{-5} torr.

Standby Pressure   5 X 10^{-8} torr.

Operating Pressure   3 X 10^{-6} torr.

Mass Spectrometer and Signal Handling

Quadrupole Analyzer	1.59-cm x 20-cm rods with alumina ceramic collars, designed for high resolution and high transmission, from Extranuclear Laboratories Inc.
Mass Range	2 to 560 amu in one continuous linear range
Mass Position Stability	Better than ± 0.1 amu over a 12-h period
Mass Linearity	Better than ± 0.1 amu over a total mass range
Mass Readout	Digital display on CRT to 0.1 amu
Start Mass	2 to 560 amu adjustable by keyboard or manual control
Scan Width	1 to 560 amu adjustable by keyboard or manual control
Zero Sweep	Function available for single ion monitoring
Time Constant	Adjustable threshold setting automatically selects the signal handling time constant with the ion pulse rate
Resolution	Adjusted by keyboard or manual control for near constant 3 M over entire mass range. Maximum of 5 M to 560 amu
Signal Handling	A pulse counting, signal handling system is used for positive and negative ion detection. Dynamic range response is 1 to 10^7 ions/s with automatic range control

Multiplier	Channeltron-type, gain 10^8 at 4 kV. Power supply switched from positive to negative ion detection by keyboard or manual control. An off-axis placement of the multiplier is standard.
Multiplier Protection	Multiplier high voltage power is automatically cut off by the system controller if a signal level greater than 10^7 ions/s is experienced by the multiplier for a period of 50 ms. The operator resets manually, as required.
Analog Output	Analog output, range 0 to 2.5 V offers a linear display of 4 decades of signal from 10^2 to 10^6 ions/s, with overrange indication between 10^6 and 10^7 ions/s. This output is for use under the manual control mode of the signal handling system.

Micro Processor

Keyboard Control	All mass spectrometer and signal handling parameters are entered through the keyboard of a VT-55FA interactive graphics terminal and copier from Digital Equipment Corp.
System Control, Data Acquisition, Storage, and Treatment	These functions are performed using a PDP-11/03 microprocessor with a 28 K semi-conductor RAM, a 483 ms average access time dual floppy disk system, and a line frequency and real-time clock.

APPENDIX B

SYNTHESIS OF 3,5-DINITROTOLUENE

1) Preparation of 3,5-dinitro-4-aminotoluene

A 1-L sample of 90% nitric acid was poured in a flask equipped
with a mechanical stirrer and a thermometer. A 100-g sample of
N-acetyl-p-toluidine (K & K Laboratories Inc., N.Y.) was added rapidly,
but in small quantities, an ice-water bath kept the reaction temperature
below 295 K. As soon as all the N-acetyl-p-toluidine was dissolved,
the mixture was poured over 1L of crushed ice to be quenched; it
was then set aside for precipitation. The yellow precipitate was
filtered and washed free of acid. The moist solid was then heated
for one hour, at 363 K, in 670 mL of 50% sulfuric acid. The cooled
reddish mixture was filtered and dried under vacuum over sulfuric
acid (96%). The crude yield was 105.3 g, or 80% (mol/mol), and its
melting point was 442 K.

2) Preparation of the 3,5-dinitrotoluene

A 28.0-g sample of 3,5-dinitro-4-aminotoluene was suspended
in a solution of 550 mL absolute ethanol and 138 mL of 96% sulfuric
acid, in a three-necked flask equipped with a mechanical stirrer.
We added 82.7-g of sodium nitrite. The exothermic diazotization
reaction caused the ethanol to reflux. This reflux was sustained
and controlled by small additions of sodium nitrite. When the reflux
and effervescence ceased, we added 500 mL of cold distilled water and
we set the mixture aside for precipitation. The precipitate obtained
was filtered and washed free of acid with three 130-mL quantities
of cold water, then dried under vacuum over Drierite (8 mesh). The
crude yield was 24.1 g or 93% (mol/mol); its melting point was 366.5 K.
We recorded the NMR spectrum to certify the product.

CRDV R-4209/81 (NON CLASSIFIE)

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"Ionisation chimique à pression atmosphérique: spectres de masse
négatifs des isomères du dinitrotoluène" (NC)
par M. Asselin et J. Paré

L'ionisation chimique à pression atmosphérique des isomères
du dinitrotoluène (DNT) a été étudiée dans l'air ambiant, à l'aide
d'un spectromètre de masse quadripolaire opérant dans le mode négatif.
Les isomères sont regroupés sur la base des ions produits: le 2,5-,
le 2,6- et le 3,5-DNT forment l'anion moléculaire avec peu de
fragmentation; le 2,3- et le 3,4-DNT se comportent de façon similaire
mais avec beaucoup plus de fragmentation; le 2,4-DNT produit l'ion
quasimoléculaire (DNT-H)⁻ avec très peu de fragmentation. Les résultats
sont interprétés en termes de structure moléculaire des isomères. (NC).

DREV R-4209/81 (UNCLASSIFIED)

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"Atmospheric Pressure Chemical Ionization Negative Mass Spectra of
the Dinitrotoluene Isomers" (U)
by M. Asselin and J. Paré

The atmospheric pressure chemical ionization of the
dinitrotoluene (DNT) isomers in ambient air was studied with a quadrupole
mass spectrometer operating in the negative mode. The isomers can be
grouped on the basis of the product ions: the 2,5-, the 2,6-, and the
3,5-DNT give the molecular anion with little fragmentation; the 2,3- and
the 3,4-DNT behave similarly but with more extensive fragmentation;
the 2,4-DNT gives the quasimolecular (DNT-H)⁻ with little fragmentation.
The results are discussed in terms of the molecular structure of the
isomers. (U)